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Siloxanes synthesized "in situ" by sol–gel process for fire control in wood of *Araucaria angustifolia*

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ABSTRACT

Panels of *Araucaria angustifolia* were chemically modified with alkoxysilanes, hydrolyzed and condensed "in situ" by the sol–gel process. Alkoxysilanes selected were aminopropyl methyldiethoxysilane (A), aminopropyl triethoxysilane (B) and a mixture of both (C). Ethanol was used as solvent in 4/1 ethanol/alkoxide molar ratio. The pH was adjusted to alkaline value for controlling the kinetic of hydrolysis–condensation reactions.

Impregnation process was carried out at 45–50 °C in an autoclave, controlling the operating conditions for achieving different weight gains.

Laboratory tests were carried out in Two-Foot Tunnel (flame spread index, panel consumption and smoke density) and in TGA detector (mass loss).

The performance in laboratory tests can be explicated according the reactivity of the alkoxides. The results support the conclusion that the best fireproof efficiency was observed in woods treated with the alkoxide B, followed by those modified with the mixture C and the alkoxide A, in this order; the results also indicates that as weight gain increased the performance of impregnants against fire.

1. Introduction

High-density woods display excellent performance against fire action since they maintain their mechanical properties longer time than steel and concrete structures [1–3].

Nevertheless, medium- and low-density woods and their sub-products (plywoods, agglomerates, laminates) are more widely used in the construction for a lot of technical and economical reasons (e.g. fast growing). These woods, without any fireproof treatment, show reduced resistance to fire penetration due to their insufficient ability to form a char insulating layer and to maintain their mechanical properties during a conflagration [4,5].

Thus, many organic (epoxies, acrylics, etc.) and inorganic substances (silicates, borates, polyphosphates, etc.) were employed as impregnants for giving fire resistance to medium- and low-density woods. In general, the inorganic treatments display better behavior against the fire action than organic ones due to their chemical nature (non-combustible materials). Many authors have studied the chemical modification of wood [6–10]; other authors have developed efficient flame-retardant treatments for woods applied by impregnation or as surface coating [11–13].

In previous papers, the authors studied the flame-retardant performance in low-density woods impregnated with soluble-alkaline silicates; after finishing the impregnation with silicates, the process requires the subsequent treatment with acid for promoting the silicification and with metallic salts for producing the insolubilization with the object of avoiding that the impregnant is leached from the wood during exposure to environment (in the treated wood, it would cause the loss of its resistance against fire action). In these cases, it was not determined whether the good performance achieved was mainly due to chemical or physical changes or else to both simultaneously [14–16].

In this research, the authors continued the study of inorganic impregnants derived from silicon for giving adequate protection against fire action to panels of *Araucaria angustifolia*. For this purpose, environmentally friendly alkoxysilanes, hydrolyzed and condensed "in situ" by the sol–gel process, were selected because they would react with certain components of wood, and in addition, they could be impregnated in a single stage decreasing the costs of process.

2. Materials and methods

The experiments included (i) preparation of test specimens, (ii) cellulose activation with alkaline solution, (iii) selection of

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alkoxysilanes as wood impregnants, (iv) choice of conditions for hydrolysis–condensation reactions and for aging, and finally (v) adjustment of the operative conditions of impregnation process.

2.1. Preparation of test specimens

Samples of *A. angustifolia*, free of defects, were prepared with $6\times100\times605$ mm^3 size (radial × tangential × longitudinal) for evaluating the thermal behavior and the efficiency against fire action.

2.2. Cellulose activation

Wood basically consists of three polymeric materials (cellulose, hemi-cellulose and lignin), which have a lot of hydroxyl groups. Those hydroxyl groups in lignin have high reactivity to chemical agents while in the case of cellulose the accessibility (reactivity) depends substantially on whether its structure is crystalline or amorphous.

The above bases the previous activation of the cellulose. Although various methods have been developed (e.g. enzymes, controlled microorganisms, etc.), alkaline solutions of sodium hydroxide are still widely used.

In this experiment, the specimens were pretreated in a modified Soxhlet extractor for 2 h with a solution of sodium hydroxide (pH 8.5) and then for about 5 min with distilled water for removing the alkali remaining on surface.

Then, the samples were exposed in a chamber under controlled temperature and humidity conditions (20 ± 2 °C and 60 ± 5% RH) until reaching the equilibrium moisture according to the guidelines of ASTM D 4933.

2.3. Selection of alkoxysilanes as wood impregnants

Alkoxysilanes selected were aminopropyl methyldiethoxysilane (chemical formula, $C_8H_{21}NO_2Si$; molecular weight, 191.3; aspect, clear liquid; density, 0.916 g cm^{-3}) and aminopropyl triethoxysilane (chemical formula, $C_9H_{23}NO_3Si$; molecular weight, 221.4; aspect, clear liquid; density, 0.956 g cm^{-3}); in this experiment, a mixture of aminopropyl methyldiethoxysilane and aminopropyl triethoxysilane was also used in 50/50 ratio w/w. It is worth mentioning that the selected alkoxides exhibit low toxicity and are not polluting to the environment.

2.4. Choice of conditions for hydrolysis–condensation reactions and for aging

The sol–gel process involves successive reactions of hydrolysis and condensation generating high molecular weight polymers [17–23].

An alkaline medium was chosen as catalyst; thus, the pH was adjusted prior to impregnation with ammonium hydroxide (pH 8.2 ± 0.1), Appendix A.

The alcohol is not only a solvent since its molecular weight regulates the speed of evaporation and consequently the kinetics of sol–gel process (reversible reactions). In the present experiment, alkoxides were solubilized in ethanol (4/1 ethanol/alkoxide molar ratio).

To avoid the formation of cracks during aging (stress caused by the capillary forces associated with liquid–vapor interface), the drying process was carried out at very low speed by storing the panels in laboratory conditions for three weeks.

2.5. Adjustment of the operative conditions of impregnation process

The impregnations were carried out at 45–50 °C in an autoclave under controlled operating conditions. In all cases, the 3/1 ratio v/v impregnating solution/wood was selected for ensuring that the test panels were completely submerged during the entire process.

Then, the autoclave was charged with the pretreated panels; a vacuum of 200 mm Hg was applied for 10 min for releasing air and water vapor from the cells and for facilitating the penetration of impregnant.

The corresponding alkoxide solution was added without decreasing the vacuum level. The operative conditions were adjusted for achieving different weight gains of the impregnant: the pressure was gradually increased from 1.5 to 6.5 kg cm^{-2}; this stage lasted from 15 to 120 min. The next one was the application of a slight vacuum (about 50 mm Hg for 10 min) for removing the excess alkoxide on the panel surface.

Finally, the panels were removed after reaching atmospheric pressure and then exposed into a chamber under controlled temperature and humidity conditions (20 ± 2 °C and 60 ± 5% RH) for three weeks for allowing the gelation (hydrolysis–condensation reactions) and the aging (natural drying).

The weight gain was determined for each sample by using the following equation:

$$\text{Weight gain, \%} = [(Wm - Wo)/Wo] \times 100$$

where Wo and Wm are respectively the weight of the panels pretreated in the Soxhlet and the weight of those treated in the autoclave (all of which were previously dried in an oven at 100 ± 3 °C up to constant weight).

3. Laboratory tests

3.1. Evaluation of thermal behavior

Wood panel with prior cellulose activation (control panel) and those treated by impregnation with alkoxides after gel formation and aging "in situ" were tested in a Shimadzu TGA-50H detector (wood amount, about 5 mg; heating rate, 10 °C/min in static air atmosphere) for performing the thermogravimetric analysis (TGA).

3.2. Determination of performance against fire

In this study, the tests were carried out in a Two-Foot Tunnel (Atlas Electronic Devices Company, Model TFT, Serial No 1000, USA), under guidelines of ASTM D 3806 Standard.

The Flame Spread Index FSI was computed by using the equation $FSI=(Ls-Lo)/(Lb-Lo)$, where Ls is average of the three highest flame-advances on experimental panels, Lo is average of the three highest flame-advances on asbestos–cement board and Lb is average of the three highest flame-advances on control panel. It is worth mentioning that the value Lo is the flame-advance produced by the reflection of flame of Bunsen burner on asbestos–cement board during testing in Two Foot Tunnel; in the experiment, Lo was 50 mm.

In addition, the Panel Consumption PC was also carried out. PC represents directly the weight loss during the test and indirectly the resistance to fire penetration.

Finally, the Smoke Density SD was measured (device includes a chimney, a light source and a photocell in the opposite point of ignition); the direct reading in percent (0.0–100.0) of light transmission received in the photocell was recorded (an opaque card was used for calibrating the zero value of scale). The maximum values were registered during the test.

Table 1
Weight gain of chemically modified panels.

Alkoxide	Weight gain, % w/w	Sample
A, aminopropyl methyldiethoxysilane	2.28 ± 0.38	A.I
	6.03 ± 0.29	A.II
	9.89 ± 0.43	A.III
	12.98 ± 0.68	A.IV
	16.21 ± 0.99	A.V
	19.42 ± 1.01	A.VI
B, aminopropyl triethoxysilane	2.61 ± 0.28	B.I
	6.45 ± 0.33	B.II
	10.05 ± 0.43	B.III
	13.63 ± 0.55	B.IV
	16.62 ± 0.39	B.V
	18.75 ± 0.66	B.VI
C, aminopropyl methyldiethoxysilane/aminopropyl triethoxysilane(50/50 w/w)	2.80 ± 0.24	C.I
	6.61 ± 0.36	C.II
	10.33 ± 0.46	C.III
	13.42 ± 0.68	C.IV
	16.78 ± 0.55	C.V
	20.02 ± 0.78	C.VI
Control	0.00	D

Table 2
Results of flame-retardant tests.

Sample	FSI	PC, %	SD, %
A			
I	0.71	5.60	38.0
II	0.52	4.43	51.0
III	0.38	3.59	62.5
IV	0.27	2.62	70.5
V	0.19	2.32	76.0
VI	0.18	2.29	75.5
B			
I	0.72	5.52	39.0
II	0.43	4.01	57.0
III	0.26	3.05	68.0
IV	0.18	2.47	74.0
V	0.13	1.95	79.0
VI	0.12	1.92	79.5
C			
I	0.73	5.54	39.0
II	0.47	4.19	53.5
III	0.31	3.29	64.5
IV	0.22	2.50	72.5
V	0.17	2.08	77.5
VI	0.15	2.06	78.0
Control panel	1.00	8.55	5.0

To interpret the influence of main effects, results were statistically treated according to the following factorial design: 3 alkoxides (A, B and C) × 6 weight gains (I, II, III, IV, V and VI), that is 18 panels manufactured in duplicate. The variance was calculated and then the Fisher *F* test was run. The reference tables [24] indicate that the considered variables showed an important influence on performance against fire.

For the statistical analysis of the flammability tests as a whole, in a first stage the values of FSI, PC and SD (Table 2) were turned into a scale with values from 0 to 10, which were assigned to 1.00 and 0.00 for FSI; to 8.55% and 0.00% for PC and to 5.0 and 100.0% for SD (1.00 for FSI, 8.55% for PC and 5.0% for SD correspond to control panel). The value 10 interprets the best behavior in each test; intermediate values were proportionally considered.

3.3. *Characterization of solid wood panels by FT-IR*

Details of this test and analysis of spectra are included in Appendix B.

4. Results and discussion

Table 1 displays the weight gain of the panels after gel drying (xerogel formed in the pores of the wood). The average value of minimum and maximum weight gains (retention values, quantity of solids by wood volume unit) were about 12.8 and 97.0 kg m^{-3}, respectively.

4.1. *Evaluation of thermal behavior*

Fig. 1 displays the performance of the thermal degradation of the original wood previously treated with sodium hydroxide solution. In this figure, it is noted that the panels exhibited a rapid mass loss in the 250–450 °C range. At 500 °C, the mass loss was approximately 95%, indicating that the sample burnt almost completely.

For the minimum weight gain of the three impregnants, it is not observed a substantial difference in the initial temperature of decomposition for treated samples in comparison with control panel: values for wood modified with the reactive impregnants A, B and C showed respectively an initial temperature of decomposition of 250, 260 and, finally 255 °C, Fig. 2. Concerning final temperature of fast decomposition, it was slightly lower for treated woods than for control panel (400, 390 and, finally 410 °C, respectively for impregnants A, B and C), which led obviously to a lower mass loss (e.g. 78, 68 and, finally 72% at 500 °C, respectively).

In all cases, TGA analysis indicates that as weight gain increased the performance for the three impregnants improved, Fig. 3. Thus, for the highest weight gain, it was verified a substantial increase in the initial temperature of decomposition and a significant decrease in mass loss. For example, the wood modified with impregnants A, B and C showed the following values of mass loss at 500 °C and of initial temperature of decomposition: 45% and 328 °C, 40% and 352 °C, and finally 42% and 343 °C, respectively.

Fig. 3 also displays that the range of fast thermal decomposition was significantly lower in all samples treated with the highest weight gain than control.

The above-mentioned results support the conclusion that the best performance was observed in woods treated with alkoxide B, followed by the modified ones with mixture C and finally by those with alkoxide A.

The different reactivity of the alkoxides could explicate the performance in thermal analysis. Thus, for example, the alkoxide B would present the highest reactivity since in its molecular structure has three ethoxide groups, which hydrolyzing for giving silanol groups participating in condensation reactions; on the

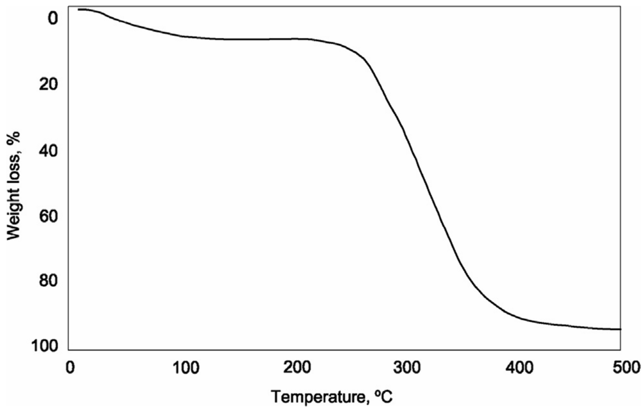

Fig. 1. Thermal degradation of wood pretreated with sodium hydroxide solution (control).

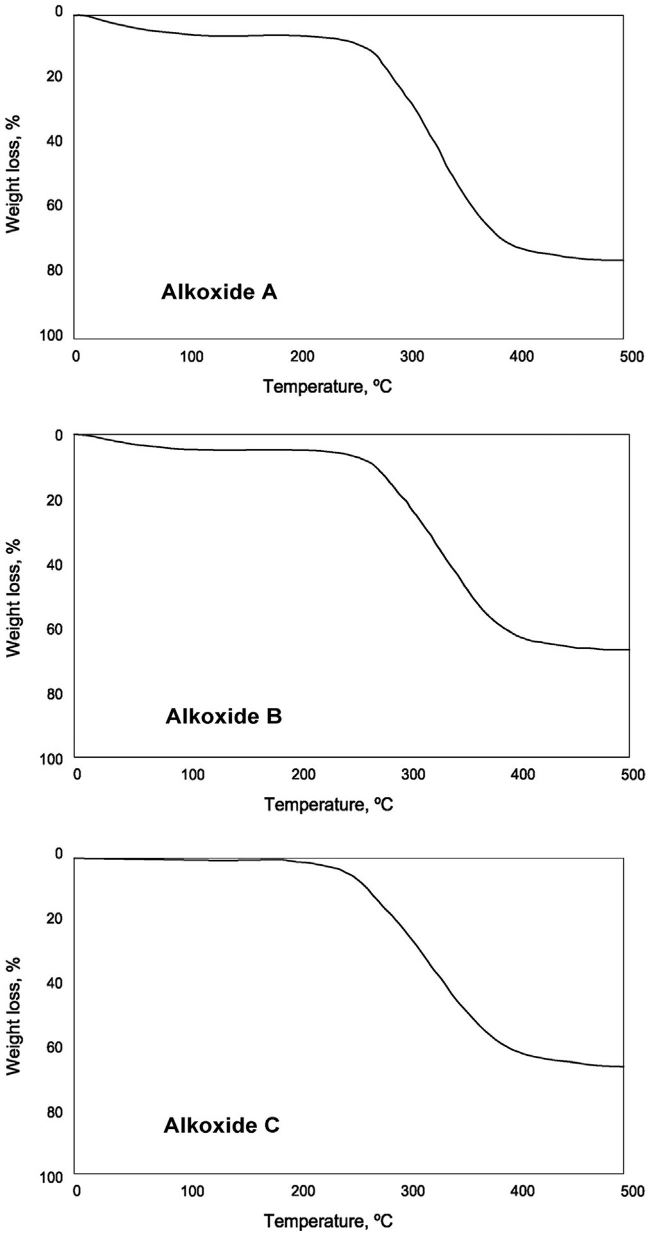

Fig. 2. Thermal performance of wood modified with alkoxides A, B and C for the lowest weight gain (2.28, 2.61 and 2.80 % w/w, respectively).

other hand, the alkoxide A has only two hydrolyzable ethoxy groups while alkoxide C would be in an intermediate position.

In addition, the rising thermal stability of treated samples with weight gain would be also based on the major amount of polysiloxanes introduced in the wood pores (e.g. 20% in the case of samples with the highest weight gain).

4.2. Determination of performance against fire

Results of flammability tests are included in Table 2. A global analysis of FSI, PC and SD indicates an improved performance of all treated panels compared with control one as well as a marked influence on fireproof efficiency of the alkoxides selected as chemical modifiers and of the weight gains produced by impregnation in the wood pores.

With the aim of determining the performance of the studied variables, the average of main effects was calculated (all of them on a scale ranging from 0 to 10), Table 3; the best performance corresponds to the highest average value.

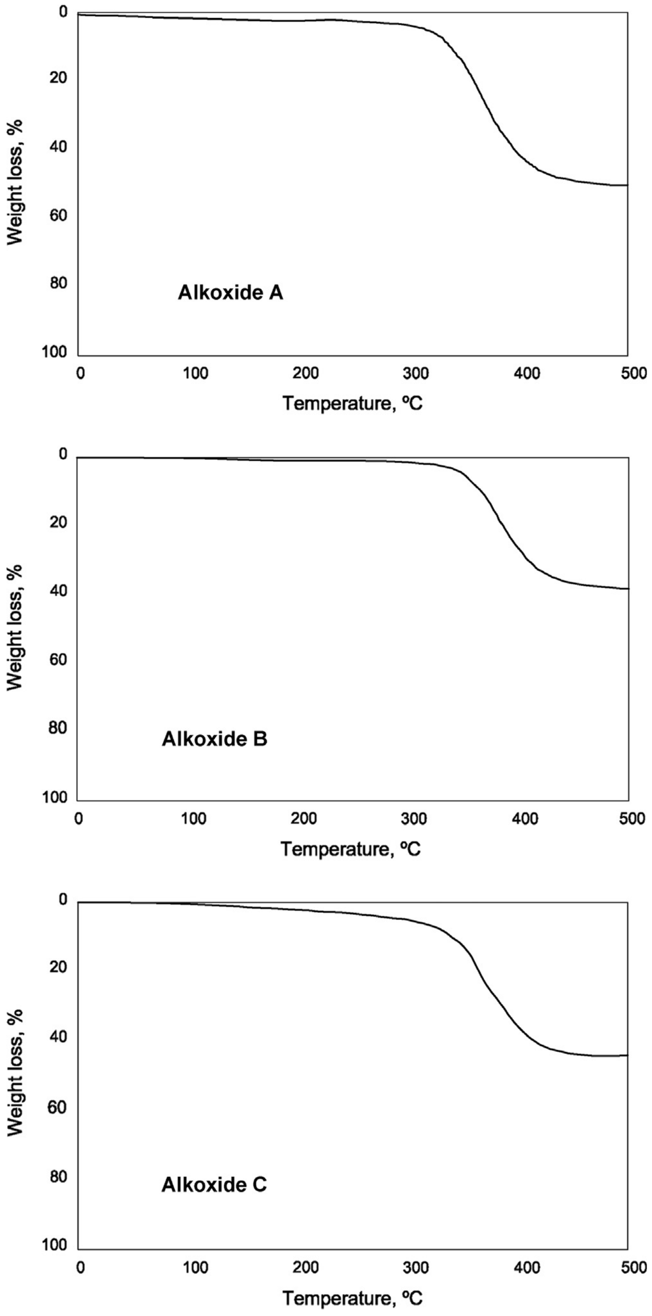

Fig. 3. Thermal performance of wood modified with alkoxides A, B and C for the highest weight gain (19.42, 18.75 and 20.02 % w/w, respectively).

A more detailed analysis indicates a difference in fireproof efficiency between the modifiers selected. For all weight gains achieved in the impregnation of wood, the highest performance was recorded with the alkoxide B (average value 6.6), then with the alkoxide C (average value 6.3) and finally with the alkoxide A (average value 6.0). The quoted different reactivity of the alkoxides could explicate the performance in fire test; this correlates with the results of the TGA.

Concerning weight gain, the increase of its value led to a better performance for the three modifiers; it is noteworthy that for V and VI levels, fireproof performance was equal in woods treated with alkoxide A (average value 7.6), also equal when alkoxide B was used (average value 8.1) and similar in those impregnated

Table 3
Average values of main effects corresponding to results of flammability tests.

Sample	Average (weight gain per alkoxide)	Average (alkoxide type)
A.I	3.3	6.0
A.II	4.8	
A.III	5.7	
A.IV	7.0	
A.V	7.6	
A.VI	7.6	
B.I	3.3	6.6
B.II	5.5	
B.III	6.8	
B.IV	7.5	
B.V	8.1	
B.VI	8.1	
C.I	3.3	6.3
C.II	5.2	
C.III	6.4	
C.IV	7.3	
C.V	7.8	
C.VI	7.9	
Control panel	0.0	0.0
Weight gain level	Average	
I	3.3	
II	5.2	
III	6.3	
IV	7.3	
V	7.8	
VI	7.9	

with alkoxide C (average values 7.8 and 7.9, respectively for two quoted levels). Accordingly, for technical and economic reasons, it is convenient to select the level V of weight gain achieved in the impregnation process.

In summary, samples impregnated with alkoxide B (in the two highest levels of weight gain) showed the best average performance in flammability tests carried out. This is based on that the Flame Spread Index (FSI$=$0.12) was really very low, which implies a net advance of flame of only about 67 mm beyond the advance produced by the reflection of the flame on asbestos–cement board (control panel burned along its 605 mm length), on that the Panel Consumption (CP$=$1.92%) was also very low (the loss of control panel was 8.55% in weight), and finally on that the Smoke Density (SD$=$79.5%) was also very low (control panel showed a light transmission of just 5.0%).

It is worth to mention that the quoted results acquire significance (i.e. the low flame spread, the high resistance to fire penetration and the low smoke generation) because they are the most appropriate conditions during a conflagration for allowing the fastest and safest evacuation of people and the protection of materials.

Studied systems would have the following flame-retardant mechanism: (1) the polysiloxane phase would isolate the underlying material retarding its degradation kinetics, (2) the highly-stable and chemically-formed hybrid interface between wood and polysiloxanes would also contribute in fireproofing performance (average dissociation enthalpies ΔH° of $\equiv$Si–O– and –O–C$\equiv$ are respectively 460 and 357 kJ mol^{-1}) and, finally (3) the organic material would form the known retardant residue (char) before that the interface and polysiloxanes are exposed again.

5. Conclusions

- Polysiloxanes synthesized inside the wood pores by the sol–gel process, by using aminopropyl methyldiethoxysilane, aminopropyl triethoxysilane and aminopropyl methyldiethoxysilane/aminopropyl triethoxysilane mixture in 50/50 ratio w/w as precursors, proved to be efficient as fireproof impregnants for panels of *A. angustifolia* in tests carried out in Two Foot Tunnel and TGA detector.
- The results indicate that the best performance was observed with wood treated with aminopropyl triethoxysilane, followed by those modified with a mixture of both alkoxides and with aminopropyl methyldiethoxysilane, in this order; the different reactivity of the alkoxides bases the results obtained.
- For all impregnants, results of fire tests improved significantly with the weight gain of alkoxides hydrolyzed and condensed inside the wood pores; technical and economic studies should define the most appropriate level for each condition of use of the modified wood.
- Results reached in thermal analysis and flammability tests are based on the reactivity of alkoxides forming an inorganic polymer and an organic–inorganic interface in wood pores; the formation of condensation bonds such as $\equiv$Si–O–Si$\equiv$ within the inorganic polymer and $\equiv$Si–O–C$\equiv$ at the polysiloxane–wood interface are the responsible of the high thermal stability of treated woods.
- The authors consider necessary to verify the performance of designed flame-retardant systems due to the wide variety of standardized available methods, which provides only comparative results according to test variables (size and position of the specimen; type, quantity and time of incidence of the applied energy; etc.). Consequently, the authors are conducting other laboratory tests (Oxygen Index, Cone Calorimeter, Thermal Conductivity, etc.).

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Appendices

Appendix A: pH of the solution in sol–gel process

Since this variable influence significantly on the polymerization kinetic, it is important to mention that in catalysis acidic (pH below the isoelectric point), the hydrolysis rate is rapid. With respect to the condensation reaction, as the acid concentration increases (partial protonation of the –OH groups of silanol) it is observed an increase in the overall speed of the reaction (lower sol stability and consequently more reduced gel time).

In basic catalysis (strongly alkaline pH), the hydrolysis rate is also relatively fast. With respect to the condensation reaction, as the alkali concentration increases it is observed a rapid partial deprotonation of the –OH groups of silanol, resulting in a decrease in the overall speed of the reaction (enhanced sol stability and therefore higher gel time).

To prepare high-density gels, it is not recommended a high kinetic of hydrolysis and condensation reactions since many $\equiv$Si–OH and/or $\equiv$Si–OR groups may remain trapped (difficult condensation due to steric hindrance).

Alkaline medium chosen as catalyst lead to the formation of aggregates (clusters), which are then linked to form a single large aggregate called gel. After gelation, the system continues producing nano-structural and chemical changes (aging). Finally, the system contraction takes place because of the expulsion of liquid phase contained in the wood pores (water and alcohol, products of hydrolysis–condensation reactions); this leads to hardening of the gel (xerogel).

Appendix B: Assessment of chemical modification

Wood panels, cut with a microtome provided with a biplane blade (angle sharpened, 30°) and dried at 100/105 °C, were analyzed by Fourier Transform-Infrared Spectroscopy (FT-IR) for determining the chemical modifications after finishing the described treatments.

The spectra were obtained by using a Perkin Elmer (model Spectrum One; method of Attenuated Total Reflectance, single rebound); the equipment consists of a zinc selenide viewer and a diamond crystal as an interface between the sample and infrared radiation.

Fig. B.1 shows the FT-IR spectra of wood before and after activation of the cellulose; it can be observed the characteristic vibrations of the aliphatic bonds ≡C–H and in addition, the asymmetric and symmetric vibrations of the groups $-CH_3$ and $=CH_2$ (between 600 and 1000 cm^{-1}) as well as the typical band of –OH group around 3400 cm^{-1} belonging to organic compounds such as cellulose, hemicellulose and lignin. Activation is evident in this last peak since the intensity increases due to the greater availability of –OH [25].

Furthermore, Figs. B.1 and B.2 show respectively the infrared spectra of woods modified with alkoxides A, B and C, for the highest weight gain considered. Initial analysis indicates that the spectra are markedly different, which indicates that chemical changes were generated during polymerization in the pores of the wood.

The above figures display bands around 1050 cm^{-1}, which could be assigned to ≡Si–O–Si≡ of the inorganic polymer formed by the hydrolysis and condensation reactions. They also allow the observation of bonds around 1120 cm^{-1}, which could be attributable to ≡Si–O–C≡ formed from the hydrolysis of alkoxides and subsequent condensation of silanol groups with the –OH groups of the wood.

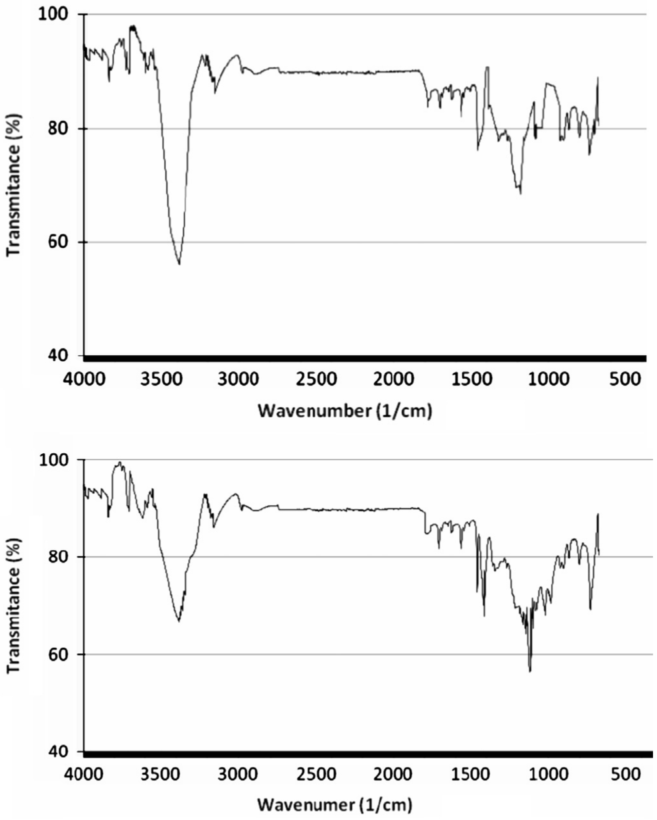

Fig. B.1. FT-IR spectra of wood before (upper) and after (lower) cellulose activation.

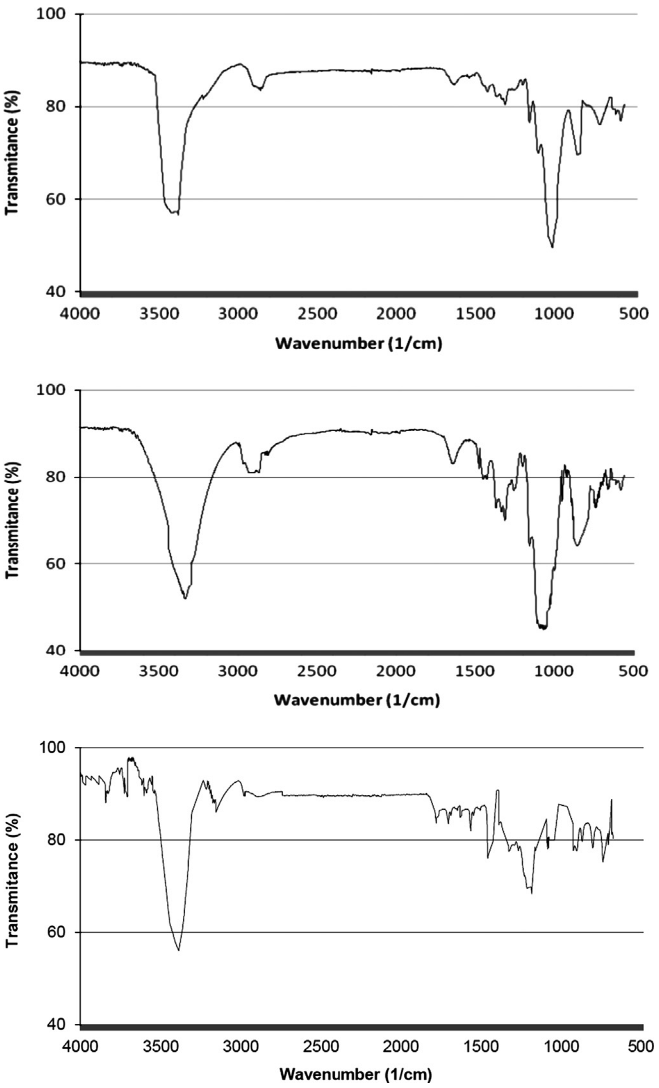

Fig. B.2. FT-IR spectra of wood modified with alkoxides A (upper), B (medium) and C (lower).

In addition, Figs. B.1 and B.2 display the bands at 1260 and 800 cm^{-1}, which could be assigned to $\equiv Si{-}CH_3$ of alkoxides when polymerized [26].

With respect to signal to the 3400 cm^{-1} (typical of the –OH groups), it is worth mentioning that in wood treated with alkoxides A and B, it was not observed a decrease of intensity of signal in spite of condensation reactions verified between hydrolyzed alkoxides and –OH groups of wood (typical absorption of ≡Si–O–C≡ around 1120 cm^{-1}). It would be based on the masking generated by ≡NH groups of alkoxides (these vibrate at same wavelength that –OH); even, for the reason above-mentioned, it was noted an increase of the peak at 3400 cm^{-1} in Figs. B.1 and B.2 [27–29].

Following with the analysis of peak at 3400 cm^{-1}, it is observed a significant decrease of this signal in the wood treated with the alkoxide C, which is attributable to the reaction of –OH groups of wood with the hydrolyzed alkoxides; it corroborates the indicated chemical modification of wood components (appearance of linkage ≡Si–O–C≡ around 1120 cm^{-1}), Fig. B.2 [30].

Furthermore, the quoted Fig. B.2 allow also observing an increase in the band intensity at 1550 cm^{-1} and the appearance of a new peak around 2900 cm^{-1}, which is attributable to that $\equiv$NH groups leave of vibrating at 3400 cm^{-1} by the generation of structures asymmetrically polymerized after the reaction randomly of both hydrolyzed alkoxides with –OH groups of wood [31].

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